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NASA WORK ON HIGH-ENERGY-DENSITY ELECTROCHEMICAL
POWER DEVICES

by

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To assure crew safety during manned space flights and to maximize the probability of success of unmanned space missions, all spacecraft subsystems must have extraordinarily high reliability. In addition, each subsystem should be as small and as light as possible, to make available a maximum of space and weight for payloads. These are the general goals of the electrochemical research and development program that aims at providing reliable, high-energy and high-power-density subsystems for space. Since the same type of criteria, together with other considerations, must be applied to automotive power plants, a number of space-oriented electrochemical projects are of terrestrial interest as well. The methods used and results obtained in these studies may find more or less direct commercial use. And even if a given space-type device is not practical under everyday conditions, the lessons learned from its development are often helpful in adapting it to meet other physical and economic requirements.

BATTERIES

Organic Electrolyte Systems

Among pertinent battery tasks is the search for high-energy-density electrochemical couples, i. e., fuel-oxidant combinations, with compatible electrolytes. For six or more years, the Army, Navy, Air Force, and NASA have sponsored in-house, grant, and contract work on the use of organic solvents with inorganic solutes as battery electrolytes. All of these efforts have shown how difficult it is to obtain highly pure cell components; and purity appears to be a requisite for compatibility. Even if this problem is solved, the fact remains that all organic electrolytes that have been investigated until now have such low ionic conductivities as to make them unsuitable for high rates of discharge. Thus, although high energy density may be achieved, high power density has yet to be shown. We can go even farther and say that an operable compact, high-power cell would have an inherent difficulty: Because no electrochemical

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reaction is 100% efficient, the rate at which heat is produced per unit volume in such a system must be higher than in a conventional one, hence calling for special engineering skill to maintain thermal control. The negative results of these efforts are valuable lessons in themselves. In addition, a potentially positive result has come from one of the contracts in this area:

Since mid-1963, Monsanto Research Corp. has been investigating their dry-type battery or fuel cell (US Pats. 3,260,620 and 3,293,080) under various NASA contracts (currently NAS3-7624). One might have a prolonged semantic discussion as to whether this is a battery or a fuel cell. Suffice it to say that the device employs a multiple-reserve construction, i. e., the active components are packaged separately and combined only immediately before use. Because of the bulk and weight of its inevitable non-active components (packaging, drive, controls, housing), the dry tape does not appear to be applicable to missions of up to 4 or 5 hours, the maximum duration of driving a conventional car before refueling. But one of the cathodic materials studied under this task has some interesting properties that make it, as well as related substances, worth further consideration. Trichlorotriazinetrione (also called trichloroisocyanuric acid) is a solid, organic bleach that contains 85% equivalent chlorine on a weight basis. In combination with magnesium, for example, the theoretical energy density of the electrochemical couple alone is 750 watt-hours per pound. A more compatible electrolyte remains to be found; and the weight of a battery would obviously be much more than that of the bare active materials. But this bleach offers the energetic advantages of chlorine without the tankage weight penalties and the toxicity hazards entailed by the use of that gas.

I should like to suggest, therefore, that bleaches be considered as oxidants in batteries or battery/fuel-cell hybrids. If an acceptable solid electrolyte can be found, a flow-through cathode might be combined with it, through which a liquid bleach, or a bleach dissolved in an inert solvent, is pumped. The light-weight storage tank for the oxidizer might contain a flexible bladder, so that the spent liquid can be stored in the same container before re-processing. The solid electrolyte must prevent diffusion of materials into the anode. The flowthrough cathode would permit continuous flushing of the cell and thus avoid undesirable build-up of products.

Alkaline Batteries

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Let menow switch from a futuristic to a more immediate electro-chemical system, the zinc-oxygen cell. A number of projects aimed

at improving the silver oxide-zinc space battery have direct bearing on that system, particularly on a rechargeable zinc-oxygen or zinc-air battery. When the zinc anode is recharged, i.e., when zinc is electroplated from the electrolyte back on the anode, it becomes covered with uneven zinc deposits. Zinc dendrites or needles tend to penetrate the cell separator and eventually to short-circuit the cell by contacting the cathode.

In a contract with the Goddard Space Flight Center (NAS5-3908), scientists at Leesona Moos Laboratories observed three distinctive types of zinc dendrites. Mossy, pine-tree shaped, or acicular deposits were formed, depending on the overpotential. The mossy kind, deposited at up to 0.1 volt overpotential, is least objectionable; but this means that zinc plates have to be recharged very slowly. Small hydrogen bubbles and local density differences between zincate-rich and zincate-depleted electrolyte caused localized convection at dendrite tips and thus contributed to undesirable needle growth. Once started, needles grew more easily than smooth deposits, because zincate ions diffused slowly; the needles "reached out" for more zinc. Needle growth was worst at the edges of electrodes. Masking the edges with non-porous polyethylene or other plastic was proposed as a solution to edge growth. Unsymmetrical pulse charging was suggested to the contractor, who did indeed find that 30%-on-60%-off resulted in lower dendrite growth than continuous charging. Thus a "half-wave" or other type of discontinuous charge may overcome some of the rate limitation set by the low overvoltage requirement for continuous charge.

A parallel effort at Yardney Electric Co. (NAS5-3873) confirmed a number of these findings. In addition, examination of zinc deposits in membranes established that they penetrate by deposition within the separator rather than by mechanical puncture. High overpotential and low zincate concentration in solution are the chief causes for such harmful growth. Furthermore, the overpotential at which penetration takes place was found to be a function of the partition of zincate ions between the adsorbed state (on separator fibers) and the free state (in solution, held within the separator). The lower the partition ratio adsorbed:free zincate, the more resistant is the membrane to zinc penetration. Although cellophane soaked in 44% KOH gave a ratio of only 0.03, it is not stable enough to be a good separator.

The best organic separator found thus far, for both stability and low zinc penetration, was prepared by the Borden Chemical Co. (NAS5-9107).

A 10% aqueous solution of methyl cellulose (700g) and a 10% aqueous solution of poly(vinyl methyl ether/maleic anhydride) (300g) were mixed at 0°C. The solution was poured on a glass plate, leveled with a doctor blade, and water was allowed to evaporate before the film was stripped from the glass. Even so, the 60 or so cycles obtained with silver oxide-zinc cells would obviously be far from commercially acceptable. Relief may come from projects that started from completely different reasons.

An inorganic separator was developed by Astropower Laboratory to operate silver-zinc cells at much higher temperatures than the normal range of about 0° to 40° C. It has been incorporated into test cells (NAS3-7639) and sustained well over 1000 cycles at 35% depth of discharge and 25°C; even at 100°C and 50% depth of discharge, it has sustained more than 250 cycles. Another inorganic separator, electrodeposited calcium hydroxide, has been studied for us by GE (NAS5-9168 and is now being further evaluated. A separator made by RAI specifically for sterilizable batteries (JPL contract 951015) still remains to be tested for resistance to zinc penetration. In principle, however, inorganic or organic high-temperature or sterilizable separators may turn out to be tougher and longer-lived under ambient conditions than their more traditional precursors.

We have started work on primary and secondary zinc-oxygen cells for space during the past fiscal year. Of particular interest are preliminary results obtained at Union Carbide Corp. (NAS5-10247), where a zinc-oxygen 16-AH secondary cell was discharged about 20% in 2 hours and recharged in 6 hours. This 8-hour cycle has been repeated 14 times thus far. Such charge/discharge times approach those one might expect for everyday battery uses.

Auxiliaries and Test Procedures

Whereas the cathode of the zinc-oxygen (air) battery is only a partial product of recent fuel-cell research, the fuel cell as a whole has been incorporated into batteries, not as a power-producing but as a gas-consuming device. Gassing of zinc plates, which evolve hydrogen with most any electrolyte under almost all circumstances, would make a sealed battery structure impossible if the gas could not be consumed again. Miniature fuel cells inserted in silver-zinc cells have operated satisfactorily for up to 1 year (NAS5-9594) and are being further

developed and evaluated by Astropower and at NASA's Goddard Center. The same purpose can be achieved by fuel-cell type auxiliary electrodes that have been used by GE (NAS5-3669), among others, to remove both hydrogen and oxygen from sealed silver-zinc cells.

The question of charge control is not simply answered; the correct method depends on the size of the power supply and on the time available for recharging, according to a GE report on contract NAS5-9193.

They recommended constant current charge for small (upto 15 watt)

nickel-cadmium power sources and 1-hour charge time; and constant voltage/coulometer cut-off with auxiliary gas-recombination electrodes for larger power supplies. -- A simple electrochemical coulometer, made from commercial cadmium plates, was described by E.R. Stroup in NASA report X-716-66-462. It works well with nickel-cadmium batteries at 0° to 25°C for at least one year. Although these charge-control devices and procedures were developed specifically for nickel-cadmium batteries, the space workhorses, I cite them because they indicate what can be done and must eventually be adapted to assure safe and reliable operation of other battery power plants.

Like all battery manufactures and many other battery users, we have our own test programs and procedures. An original contribution to this type of activity arose from a brief contract with RCA (NASW-1001) to develop statistical methods for correlating the voluminous test data. It is a non-destructive procedure for determining the quality of a battery. Though perhaps not an original discovery of Mr. J.H. Waite, (it appears to have been used on relays in WW II), it is potentially applicable to any mass-produced item and looks particularly valuable as a deterministic, instead of the usual probabilistic, statistical approach.

Briefly, the procedure is as follows: A statistically meaningful sample of a population is tested to destruction under normal operating conditions, while significant data are being recorded, particularly frequently during the initial test period. The data are manipulated to show differences, for the initial portion of the life test only, among samples that passed and those that failed for a variety of reasons. One can then take another member of the same population, obtain initial life data only, and match the results to those previously obtained, in order to predict whether this specific member will complete its mission or, if not, what will cause it to fail.

It is not yet known whether a general mathematical basis, similar to conventional statistics, can be evolved for this approach. Nor are

the physical details for meaningful battery testing fully explored as yet. Preliminary indications from nickel-cadmium battery tests are that the method may be made fail-safe; i. e., although tests showed likely premature failure, some battery packs completed their mission; but no "sound" batteries, according to prediction, failed.

FUEL CELLS

For the present, at least, NASA is concentrating on one type of fuel cell only, the hydrogen-oxygen cell with alkaline electrolyte. Although the Bacon-type intermediate-temperature (250°C) fuel cell for the Apollo spacecraft needs no added catalyst -- the nickel electrodes are catalytic enough at that temperature -- low-temperature fuel cells, up to about 150°C, do need catalysts on both anode and cathode. The greatest problem of inefficiency consists of the voltage loss at the cathode of low-temperature systems, where 0.2-0.3 volt/cell are lost as soon as any power is drawn. This is true even for the best platinum or silver electrodes.

To overcome this loss, I started a program at Tyco Laboratories in mid-1965 (NASW-1233) on preparation and screening of a series of alloys that are potential cathodic electrocatalysts. Thus far, osmium and certain titanium alloys have been identified as promising materials. They are perhaps of dubious commercial value. On the other hand, nickel carbide was found to be about 90% as good as platinum. That is not good enough for space, but in view of its price and availability it may attain commercial importance. I hasten to add that, thus far, it has been too unstable to be useful for any length of time. Similar preparations are being made for us by the Bureau of Mines (Contract W 12, 300) and being evaluated for possible ground applications by six firms. We furnish free catalyst samples to them, in return for which we obtain the test results. Since this mutual aid program has just begun, it is too early to speculate on the results.

Another problem of gas-fed fuel-cell electrodes has been with us for a long time. In 1839, Sir William (later Lord Justice) Grove mentioned, in describing the very first hydrogen-oxygen fuel cell, that the seat of the electrochemical reaction is at the 3-phase interface. He thought that power production occurs where the gaseous reactant, liquid electrolyte, and solid electrode meet. Though he was almost right, modern work has shown that the locus of reaction is just below this boundary, in a thin film of electrolyte above the visible meniscus. Gas does not react at the solid surface until after it has been dissolved in the electrolyte.

On a grant to Professor Bockris at the University of Pennsylvania (NsG 325), a graduate student has been working on the behavior of the pore of a gas-fed fuel-cell electrode, deepening the insight gained into this problem by Professor Meissner's students at MIT, Dr. Will at GE, and others. Mr. Cahan observed boiling of the meniscus in a model pore. Further work showed that about 90% of the current was produced in a meniscus ring about 10^{-6} cm thick. In other words, only about 5% of the catalyst now used in fuel-cell electrodes appears to perform its function; the rest is wasted. This study points out that extremely thin electrodes would suffice for the electrochemical reaction.

On the other hand, the thinness of the active layer may simply be the result of the way we operate fuel cells today. They are still being built according to Grove's recipe, maximizing the 3-phase interface. Suppose the active layer is so thin only because all of the sparsely soluble gas is used up in that region. Then it may be possible to improve the power density of a fuel cell by separating the two operations, gas saturation of electrolyte and electrochemical reaction, that are now so closely coupled in the electrode. This decoupling does not make sense for a single cell, but it may result in advantages for a stack of 30, 60, or even more cells. We now have three contractors taking a look at the engineering problems of novel types of fuel cells that would break with the Grove tradition. Furthermore, new work on optimization of porous electrodes is underway. In general, fuel cell power plants of today are not much more than assemblies of slightly scaled-up laboratory cells. A good deal of imaginative chemical engineering remains to be done.

But, though the core of a fuel-cell plant represents a fairly loose coalition of individual cells thus far, their combined behavior is far from that of the same number of single cells. Something always gets lost in the stacking of them, and it doesn't much matter which kind of basic building block is being used. Whereas single cells might perform well for a year or even several years, the very best stacks have only lasted for hundreds (say 1800) instead of thousands of hours so far. The reasons for failure depend on the type of cell, on the method of operation, and on the control devices, to name only the most obvious. Not enough full-size stacks have yet been built to know details about the behavior, reasons for, and methods of failure of any fuel-cell system in existence today.

The first extensive fuel-cell stack test is being carried out by Allis-Chalmers (NAS8-2696). We are doing here what has been done with batteries routinely for years. However, in view of the much higher cost of these stacks, the program now comprises only 8 of them. The stacks are being built as much alike as possible, though we will take advantage of improvements that become apparent as we go along. Each stack will be run under standard conditions for the first 200 hours to assure uniformity. After this check-out procedure, each stack will be tortured in a different manner until failure: Repeated starts and stops, simulated external short circuit, unbalanced gas pressure, improper water removal, excessive temperature, etc. The results will permit a rather modest statistical assessment of full-size stacks, their uniformity, their capability to withstand abuse, their mode of failure under different stresses, their safety and reliability. Though this is the first such systematic evaluation of fuel-cell stacks, it will have to be repeated, and on a much larger scale, if commercial uses of them is ever to become widespread. I hope that this exercise will set a helpful precedent and that many of the results and conclusions will be applicable to other than the specific system with which they will have been obtained.

Although the Allis-Chalmers system still uses ordinary asbestos to contain the electrolyte, we already know that a considerably improved material must take its place, if long-term operation of matrix-type cells is to be achieved at minimum rates of degradation. Several contractors, among them Electro-Optical Systems (NAS3-2781), are studying composite asbestos matrices or completely different substances for this purpose. In addition, Union Carbide is upgrading its free-electrolyte fuel cell for the high power and energy densities required in space (NAS3-9430). It will be interesting and instructive to compare the performance and longevity of this modified equipment with that using an electrolyte matrix, since both will be tested under quite similar load conditions.

CONCLUSION

This summary of space-oriented electrochemical R & D aimed at compact, light-weight, reliable power sources clearly shows that we have no ready-made products in the 50-100 kw class that are directly applicable to consumer uses. Yet, I hope you will agree that these ideas, approaches, data, and devices can contribute towards obtaining considerably improved batteries and fuel cells, be they upgraded conventional or radically new ones. This program should help solve

some long-standing problems, lead to simplified controls, and perhaps result in easier operability and maintainability of such power plants. We do, of course, hope that some of the concepts will end up as practical hardware that can be applied where and when electric vehicles may prove to be feasible.